Supplementary Information (SI) for Environmental Science: Nano.

Supporting Information

Elucidating the Formation of Nanoplastics from Plastic Nurdles in Hydrocarbon-Contaminated Water

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Estimation of wave power in the ocean

The wave power in shallow water in the ocean can be expressed by the following equation:

$$P = E \times C_g = \frac{1}{8}\rho g H^2 . \sqrt{gd} \quad \text{……..(Eq1)}$$

Where,

E = wave energy = $\frac{1}{8}\rho g H^2$

C_g = group velocity = $\sqrt{gd}$

ρ = density of water (1025 Kg/m^3)

g = gravitational acceleration (9.81 m/s^2)

H = wave height (m)

d = water depth

Solving for a wave height of 2 m in a 4 m deep shoreline:

$$P = \frac{1}{8} \times 1025 \times 9.81 \times (2)^2 . \sqrt{9.81 \times 4} = 31{,}494 \frac{W}{m} = 31.5 \frac{KW}{m}$$

Estimation of power in ultrasonic agitation bath

The power during ultrasonic agitation is calorimetrically determined, using the following equation:

$$Pv = \frac{C_p m \frac{\Delta T}{\Delta t}}{V} \quad \text{……(Eq 2)}$$

Where,

C_p = Specific heat of water = 4186 J/Kg.K

m = mass of liquid (Kg)

$\Delta T/\Delta t$ = rate of temperature change (K/s)

By solving the equation for 2 litres (2 Kg) of water for which the temperature of water raise from 22 °C to 36 °C in 30 minutes:

$$Pv = \frac{4186 \frac{J}{Kg.°C} \times 2\ Kg \times \frac{(36-22)°C}{1800\ s}}{0.002\ m^3} = 32{,}558 \frac{W}{m^3} = 32.5\ \frac{KW}{m^3}$$

Molecular weight calculation of HDPE by Flory-Fox equation[1]

$$M_w = \frac{2RT_m T_m^{\infty}}{\Delta H_f (T_m^{\infty} - T_m)} = \frac{2 \times 8.314 \frac{J}{mol.k} \times 406.15\ K \times 414\ K}{2409.4\ J/mol(414 - 406.15)K} = 148,000 \text{ g/mol}$$

$Gas\ constrant, R = 8.314 \frac{J}{mol.K}$

$Observed\ melting\ temperature, T_m = 133\ ℃ = 406.15\ K$

$Euilibrium\ melting\ temperature, T_m^{\infty} = 141\ ℃ = 414\ K$

$Heat\ of\ fusion\ per\ mole\ of\ repeat(-CH_2)\ unit, \Delta H_f\left(\frac{J}{mol}\right)$

$$= 172.1 \frac{J}{g} = 172.1 \frac{J}{g} \times 14 \frac{g}{mol} = 2409.4\ J/mol$$

***Table S1**: Composition of Naphtha obtained from detailed hydrocarbon analysis using gas chromatography* [2]

Method : D6729

Composite report
Total by group type & carbon number
(in mass percent)

Carbon	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Total
C4	0.020	-	0.011	-	-	0.031
C5	12.566	7.819	0.043	1.052	-	21.480
C6	12.466	16.830	0.104	8.808	1.269	39.478
C7	5.059	8.485	0.102	8.215	2.141	24.003
C8	1.471	3.957	0.564	2.450	1.327	9.769
C9	0.502	1.064	0.326	0.468	0.845	3.204
C10	0.199	0.412	0.012	0.093	0.291	1.007
C11	0.103	0.103	-	-	0.150	0.355
C12	0.065	0.035	-	0.009	0.009	0.118
Total	32.451	38.705	1.162	21.095	6.032	99.446
					Total Oxygenates:	0.005
					Total Heavies:	-
					Total unknowns:	0.549
					Grand Total:	100.000

Composite report
Total by group type & carbon number
(in volume percent)

Carbon	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Total
C4	0.024	0.001	0.013	-	-	0.037
C5	13.827	8.686	0.045	0.973	-	23.531
C6	13.010	17.641	0.103	7.958	0.995	39.707
C7	5.095	8.570	0.099	7.428	1.701	22.893
C8	1.441	3.879	0.544	2.217	1.054	9.135
C9	0.481	1.017	0.308	0.409	0.666	2.882
C10	0.188	0.386	0.011	0.079	0.228	0.892
C11	0.096	0.096	-	-	0.099	0.290
C12	0.060	0.031	-	0.008	0.007	0.105
Total	34.221	40.309	1.121	19.072	4.750	99.473
					Total Oxygenates:	0.005
					Total Heavies:	-
					Total unknowns:	0.522
					Grand Total:	100.000

***Table S2**: Final concentration and yield of NP formed in octane containing aqueous solutions from 150 mg of each type of nurdles in 15 mL of water and 150 µL of octane.*

Polymer type	*Concentration (ng/cm²)*	*Concentration (µg/ml)*	*Average concentration (µg/ml)*		*Yield (%)*	
PP	18556.50	182.13				
PP	17369.63	170.48				
PP	13825.62	135.70	162.77	±24.16	0.109	±0.016
LDPE	13785.61	135.31				
LDPE	17341.46	170.21				
LDPE	10429.66	102.37	135.96	±33.92	0.091	±0.023
HDPE	9203.19	90.33				
HDPE	8716.28	85.55				
HDPE	10961.50	107.59	94.49	±11.59	0.063	±0.008
PS	747.00	7.33				
PS	224.90	2.21	4.77	±3.62	0.003	±0.002

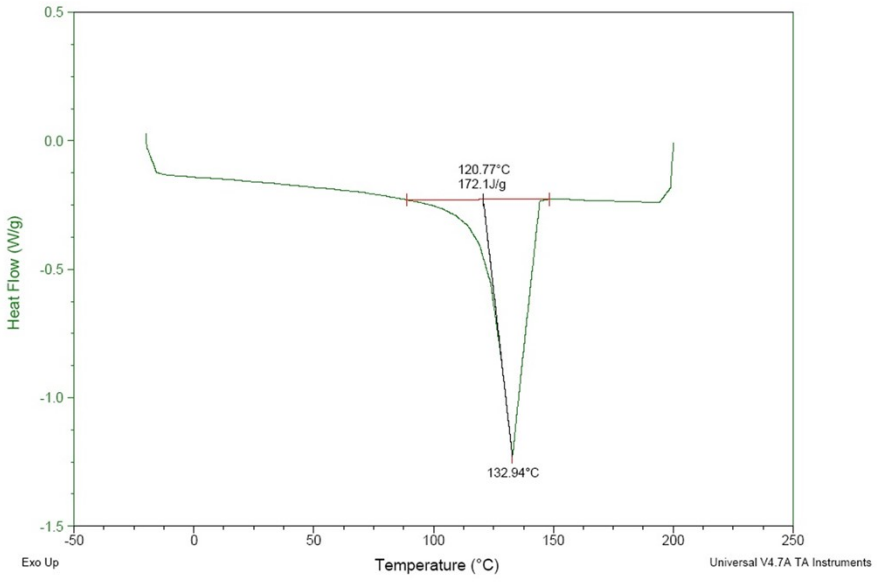

***Figure S1**: Differential Scanning Calorimetry (DSC) curve of HDPE*

Figure S2: *Photographs of emulsions produced from LDPE (left), PP (middle) and PS (right) in artificial sea water in the presence of 1% Octane.*

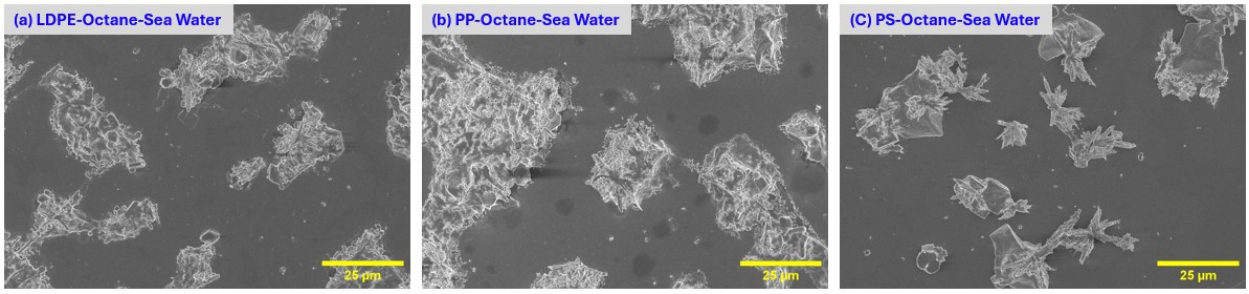

Figure S3*: SEM images of emulsion samples from LDPE (left), PP (middle) and PS (right) in artificial sea water in the presence of 1% Octane, showing predominantly aggregates of salt crystals with no discernible sMPs and NPs.*

Figure S4: *Rotary orbital shaker used for low-energy mixing.*

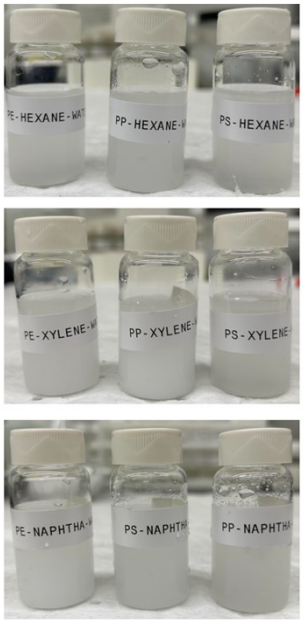

Figure S5*: Photographs of emulsions containing mixtures of sMPs and NPs of LDPE, PP, and PS in water produced in the presence of hexanes (top), xylene (middle) and naphtha (bottom).*

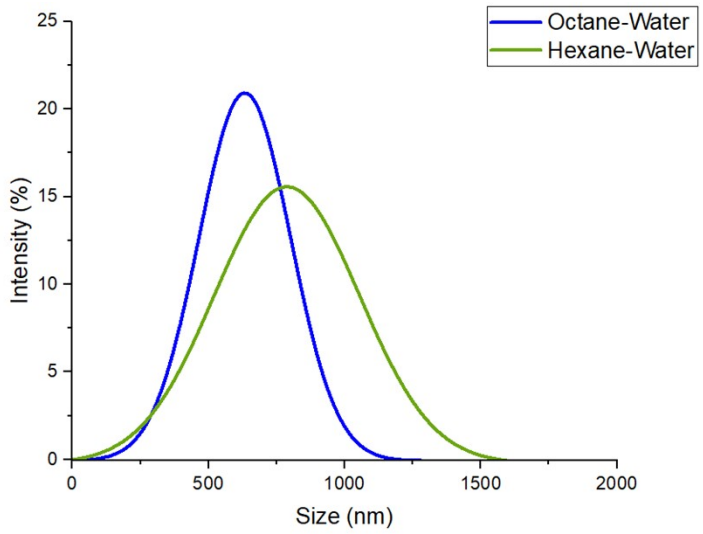

Figure S6: *Size distribution of hexane-water and octane-water O/W emulsion droplets.*

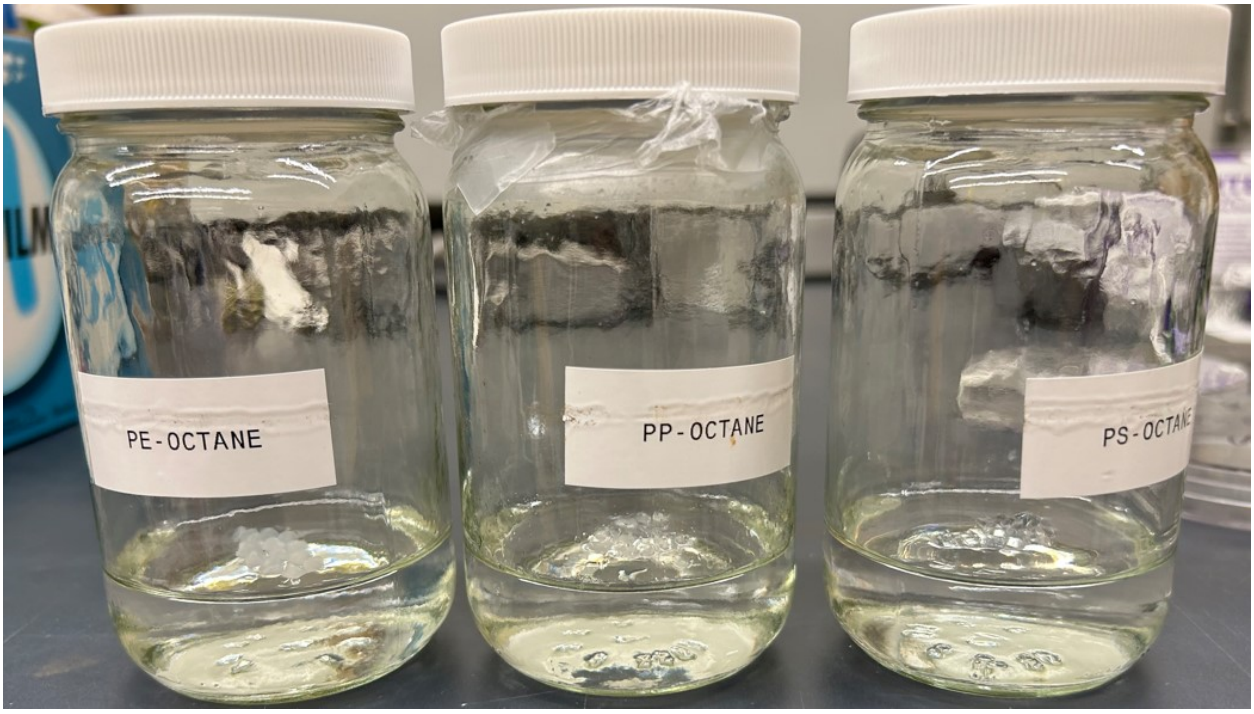

Figure S7*: Photograph of water and nurdles (PE, PP, and PS) in the presence of octane after 24 hours of rotary agitation.*

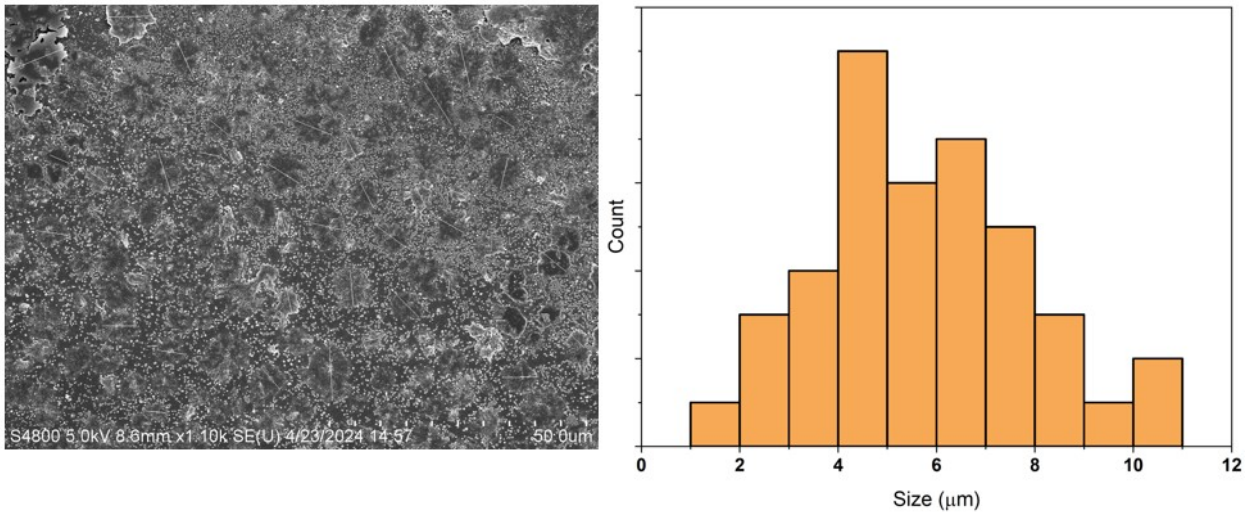

Figure S8*: SEM image and corresponding size analysis of sMPs formed in water in the presence of 1% Octane.*

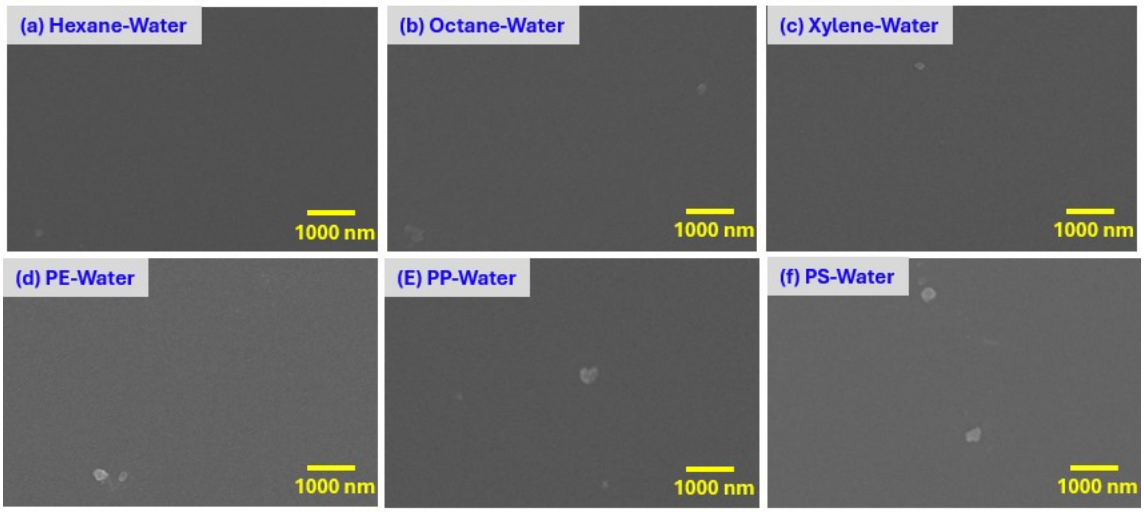

Figure S9: SEM images of control samples containing 1 vol% hydrocarbon impurities (top) and 1 wt% nurdles (bottom), prepared using ultrasonic agitation.

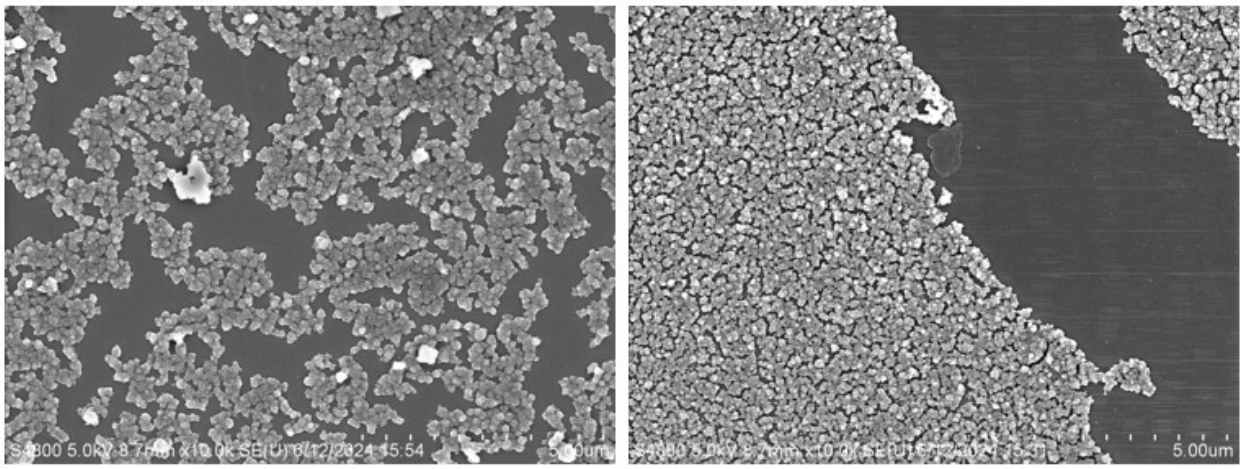

Figure S10*: SEM images of PE NPs formed in water in the presence of ~1% naphtha. Note: the image at the right side shows the NP film formation due to the aggregation on the silicon substrate upon the evaporation of water.*

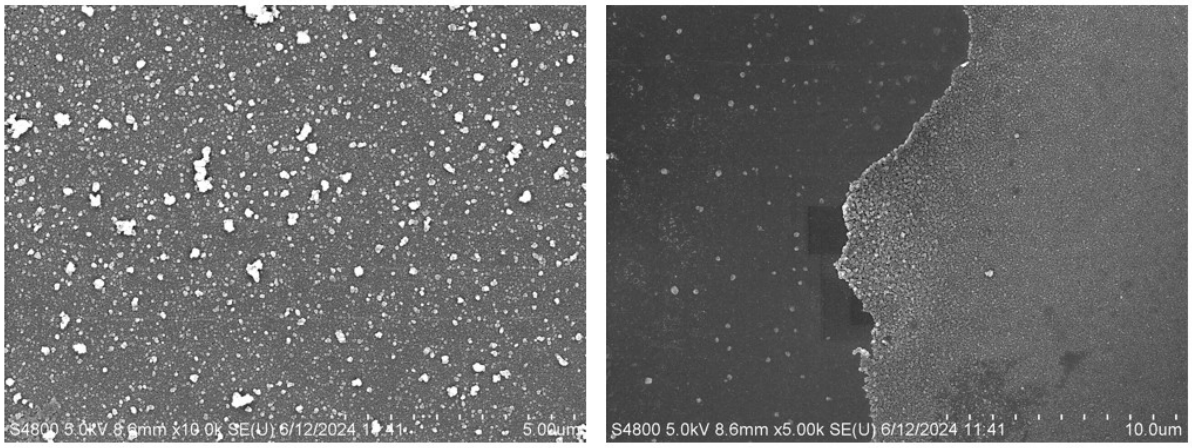

Figure S11*: SEM images of PP NPs formed in water in the presence of ~1% naphtha. Note: the image at the right side shows the NP film formation due to the aggregation on the silicon substrate upon the evaporation of water.*

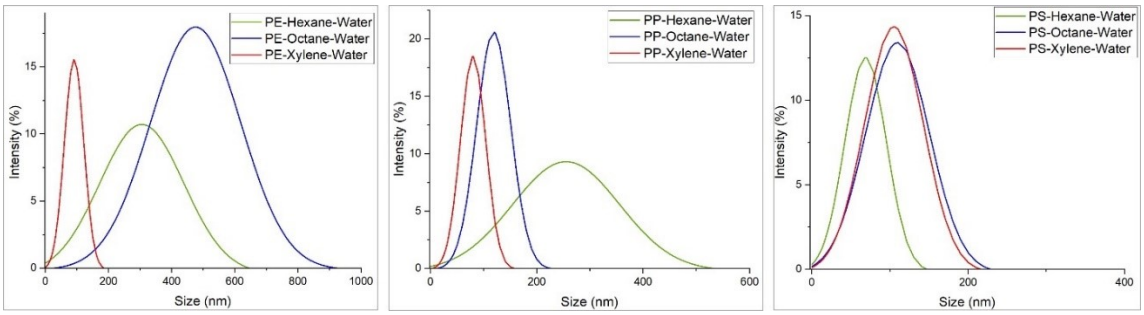

***Figure S12**: Average sizes of NPs produced in repeat experiments from LDPE (**a**), PP (**b**), and PS (**c**) in water in the presence of 1% hexane, octane and xylene, measured using dynamic light scattering.*

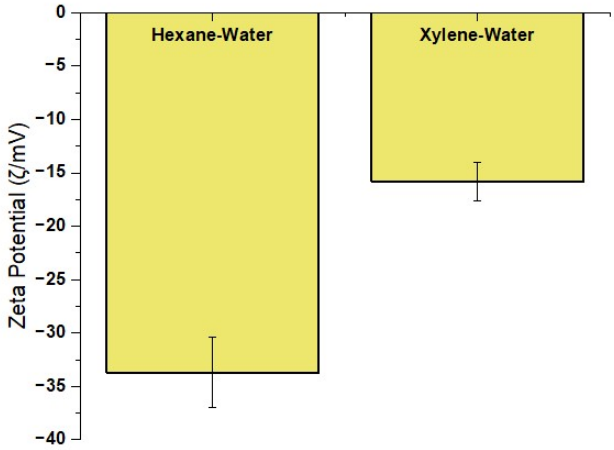

***Figure S13**: Zeta potentials of hexane-water and xylene-water-emulsions.*

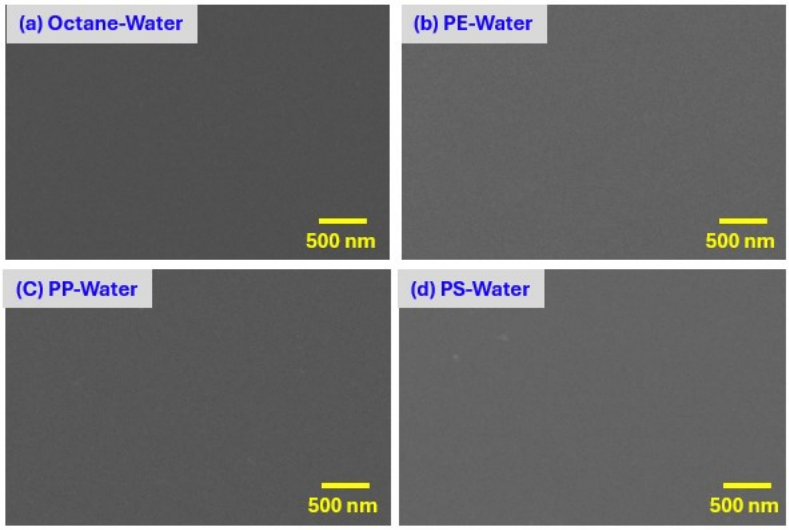

Figure S14*: SEM images of control samples containing 1 vol% hydrocarbon impurities (top) and 1 wt% nurdles (bottom), prepared using ultrasonic agitation.*

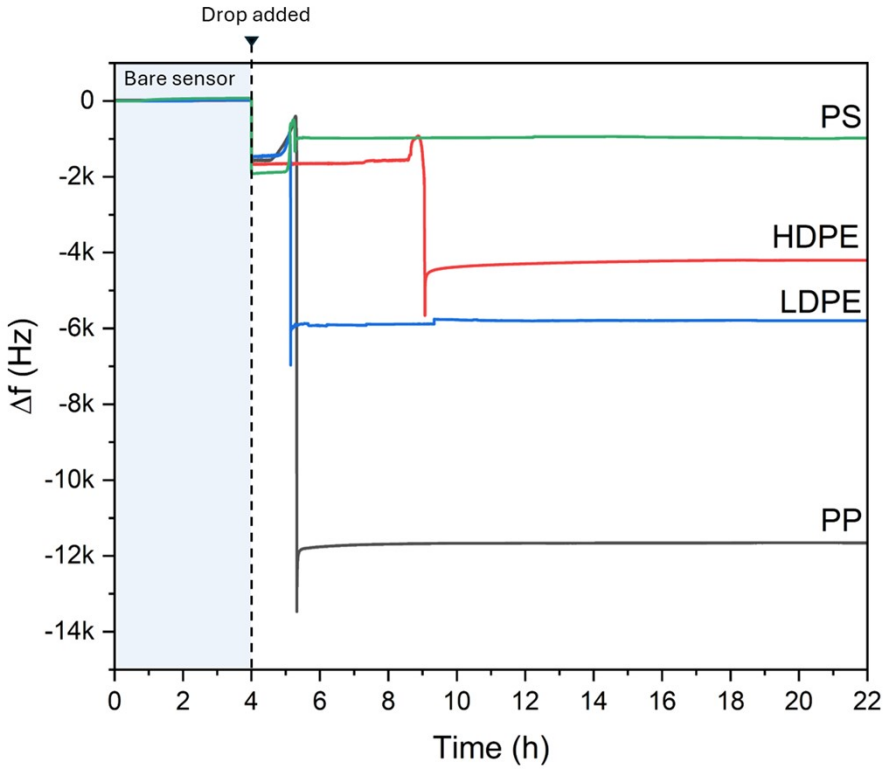

Figure S15: *QCM analysis of filtered polymer-octane suspensions after sonication. Frequency shifts (ΔF) were monitored before, during, and after adding 20 µL NP suspension on the sensor. The final frequency stabilization indicates complete evaporation of the liquid phase.*

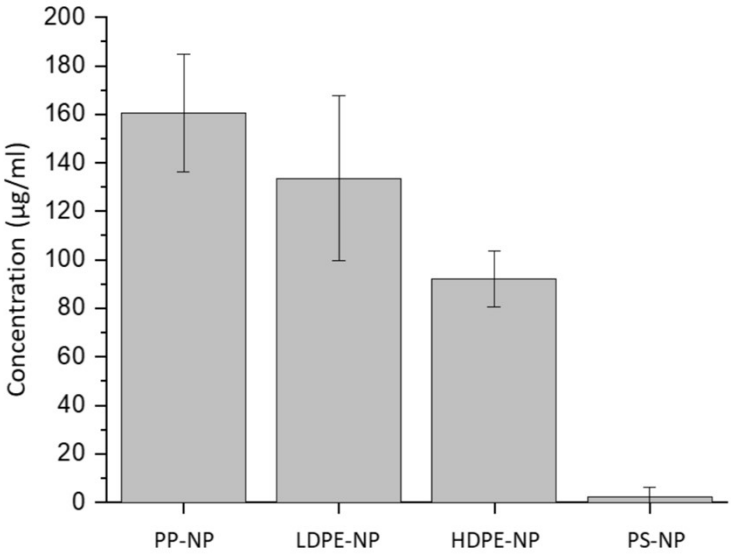

Figure S16: *Concentration of filtered NP suspensions obtained from ultrasonic agitation of 150 mg nurdles in 15 mL of water and 150 µL of octane.*

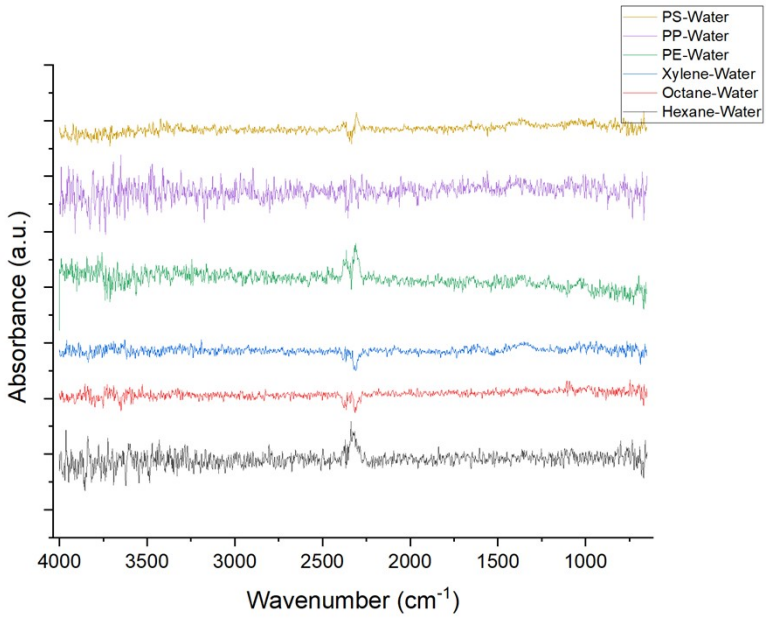

Figure 17: *FTIR spectra of control samples, prepared from the mixtures of polymer-water and hydrocarbon-water mixture.*

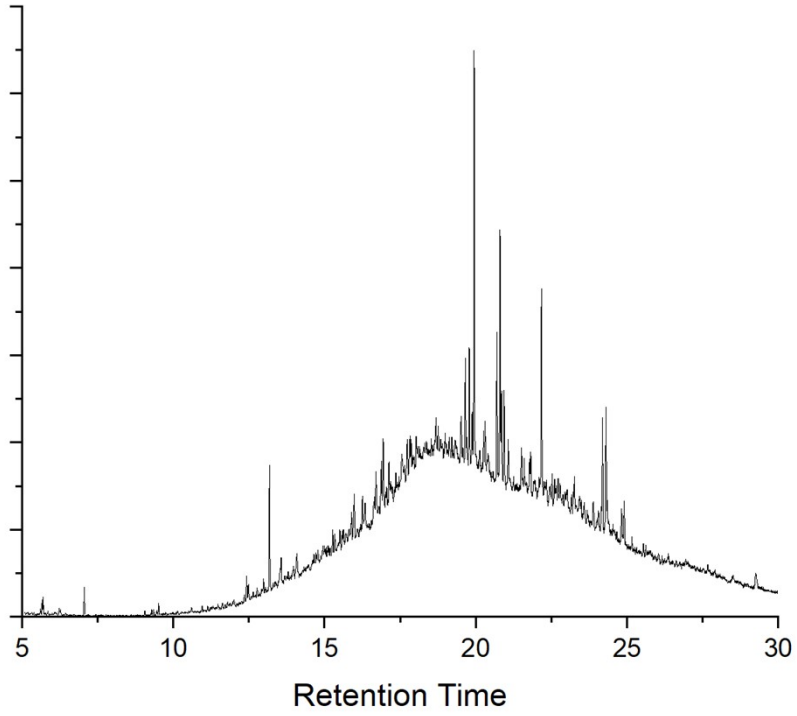

Figure S18*: Total ion chromatogram of low-density polyethylene nurdle extract in octane*

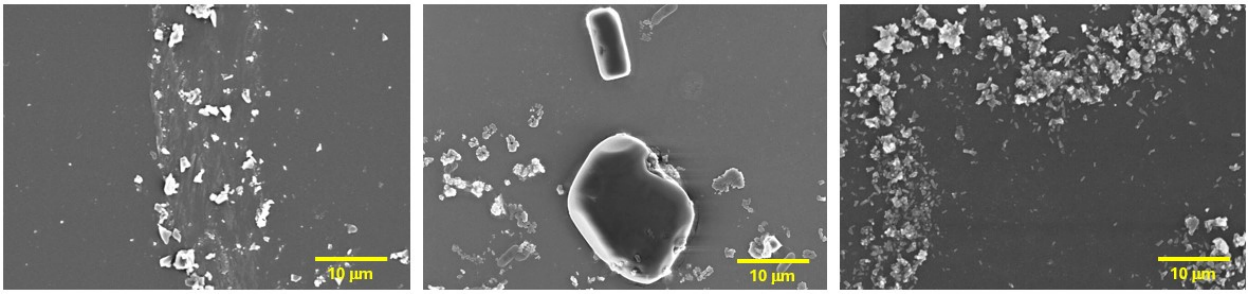

Figure S19*: SEM images of secondary microplastics (sMPs) obtained after 30 min of ultrasonic agitation of oligomer-depleted PE nurdles in water containing 1 wt% octane.*

Reference:

1. Flory, P.J. Thermodynamics of Crystallization in High Polymers. IV. A Theory of Crystalline States and Fusion in Polymers, Copolymers, and Their Mixtures with Diluents, *J. Chem. Phys.* 1949, **17**, 223-240

2. Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography, **ASTM D6729-01**, 2017